THE ROLE OF SURFACES IN THE REACTIVITY OF SOLIDS

Jerzy Haber

Institute of Catalysis and Surface Chemistry, Polish Academy
of Sciences, Kraków, Poland

Abstract - The overall mechanism of a solid state reaction
as well as texture and thus properties of the resulting
product depend on the relative rates of the development of
the reaction interface, whereat the reaction is localized,
and the reaction flux per unit area of this interface.
Variation of the reaction interface may be caused by rapid
surface spreading under the influence of surface forces
manifested in the phenomenon of wetting of one oxide by
another oxide. This results in the formation of cherry-like
grains, whose properties and reactivity are determined by
the surface layer. The reaction flux is influenced by the
presence of surface defects, which concentrate at the
surface changing its composition. Surface segregation and
formation of two dimensional phases may take place,
modifying the properties and reactivity of the surface layer.

Reactions involving solids are localized at the interface between the solid
substrate and other reactants, which may be gas, liquid or another solid.
In contrast to homogeneous reactions which proceed in the whole volume
occupied by the reacting phase, they are thus characterized by the
existence of well localized reacting zones (Ref. 1-3). The reacting zone
separates two domains filled by substances of different compositions and
properties, one of them being in the case of solid-solid reactions the
reaction product. These zones are called reaction interface. As the area of
the reaction interface changes in the course of the reaction, it must be
considered as additional variable in the kinetic equation, which may be
expressed in the form:

$$R_t \left(c_i, T, t \right) = r \left(T, c_i \right) \cdot S \left(t \right) \qquad (1)$$

where R_t is the total rate of the reaction, r is its specific rate i.e. the
rate per unit surface of the reaction interface and S is the area of
reaction interface. Both the specific rate and the area of reaction
interface are functions of surface properties of the reacting system. Thus,
by appropriate pretreatment of the surface the total rate of the solid
state reaction may be modified and the texture of the resulting product
designed in a controlled manner.

Let us first consider the variation of the reaction interface in the course
of the reaction. The influence of this factor depends on the geometry of
the reacting system: whether it is composed of pellets or whether it is a
powder mixture.

As the majority of technological processes are based on reactions in powder
mixtures, the mechanisms of reactions in such systems are of particular
interest. In the first approximation they may be considered as composed of
spherical crystallites, the reaction being localized at distinct sites on
their surface. Such topochemical reactions are characterized by the fact
that the initiation of the chemical process takes place at some defined
sites at the surface, called potential nucleation centers. The reaction
interface is visualized as the interface between crystallites of the less
mobile reactant and nuclei of the product formed at their surface at the
potential nucleation centers, to which the more mobile reactant has been
transported either through the gas phase or by surface migration. The
overall mechanism of the reaction as well as the texture and thus properties
of the resulting product depend on the relative rates of the development of
the reaction interface and those of nucleation and nuclei growth.

In the case of the powder mixture of two solid reactants, if the surface
migration or gas phase transport is much slower than the rate of nucleation
or nuclei growth, the reaction interface is formed only at the
intergranular contacts, from which it moves towards the inside of the solid
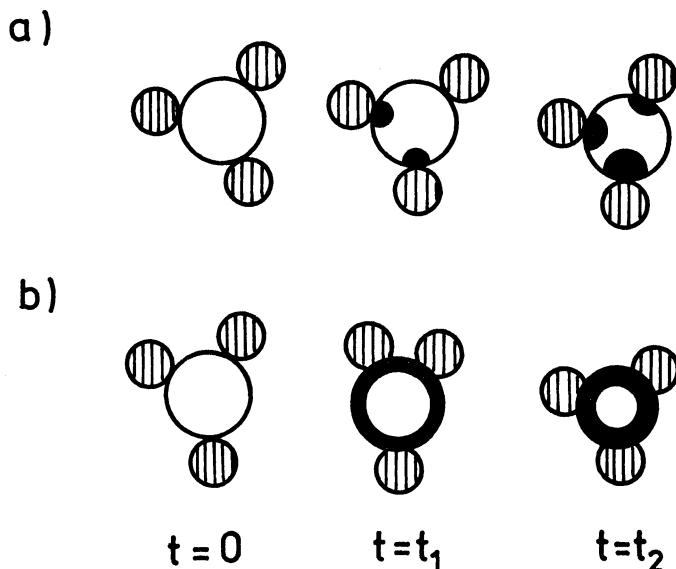(Fig. 1a).

Fig. 1 Scheme of the structure of a reacting solid state
system at three different periods of the reaction. Rate of
nucleation and nuclei growth much higher (a) or much
smaller (b) than the rate of transport of the reactant B to
the reaction interface.

The kinetic curve expressed in terms of the degree of conversion α as function of time has a sigmoidal shape (Fig. 2a), because at first the area of the reaction interface increases as it moves inwards the grains as the result of the growth of nuclei of the product until they begin to contact each other. From this moment on, the area of the reaction interface decreases and so does the reaction rate. If however, the transport of the more mobile reactant to the surface of the less mobile one is very fast, grains of the latter are rapidly enveloped by a thin layer of the former, their whole surface becoming the reaction interface (Fig. 1b). In such case the reaction interface is largest at the beginning of the reaction and decreases as the grains shrink due to the consumption of the substrate in the course of the reaction, what results in the monotonous diminution of the reaction rate with the time of the reaction (Fig. 2b).
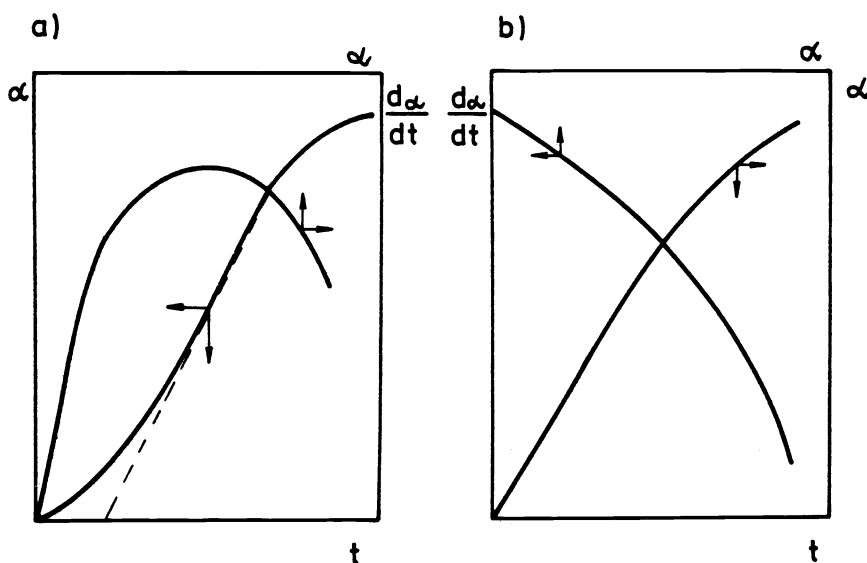

Fig. 2 Two types of kinetics observed for solid state reactions in powder mixtures.

It is usually considered that migration of one solid over the surface of another solid results from surface diffusion of constituents of the lattice under the driving force of the concentration gradient. Taking into account the relatively high values of the lattice energy of oxides one can however expect surface diffusion to be slow in the temperature range often encountered in the solid state synthesis of oxide systems.

Some time ago we have advanced a hypothesis that a different mechanism may be responsible for the rapid surface migration of solids (Ref. 4), described as wetting of one oxide by another oxide and due to the operation of the forces of surface tension. Clear manifestation of this phenomenon is the behaviour of vanadium pentoxide at the surface of two polymorphic

modifications of TiO_2; anatase and rutile (Ref. 5). Namely, when small
pellets of V_2O_5 were placed on flat discs of compressed rutile and anatase,
heated at 923 K for 48h, and separated, no changes were observed in the case
of rutile, whereas in the case of anatase V_2O_5 penetrated along the grain
boundaries into the disc of anatase to the depth of about 500 μm. Fig. 3
shows the photoelectron spectra of V2p, O1s and Ti2p electrons of the
samples of anatase, taken from the region of V_2O_5 migration, and these
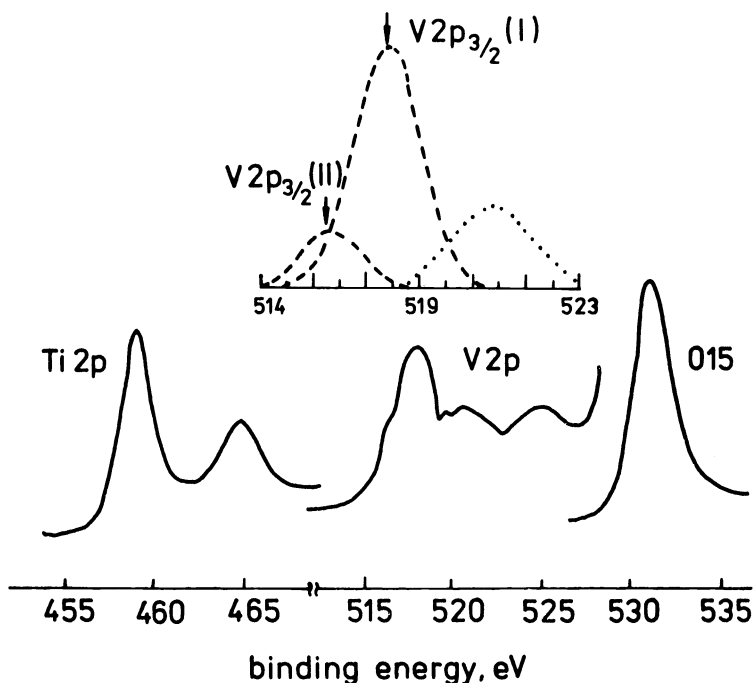spectra after computer deconvolution.

Fig. 3   Photoelectron spectrum in the region of the V2p, O1s
and Ti2p core levels (solid line) of the sample of anatase
after being contacted with V_2O_5. Dashed and dotted line show
the result of deconvolution (Ref. 5).

Two doublets of V2p electrons are visible hinting to the presence of two
types of vanadium ions: V^{+5} ions in the enviroment similar to that in V_2O_5
(form I) and V^{+3} ions in the enviroment strongly modified in comparison with
pure vanadium compounds (form II). The Ti2p doublet and O1s peak are single.
Fig. 4 illustrates the in-depth concentration profiles obtained by
sputtering with argon ions for different periods of time. The intensity of
Ti2p peak grows with sputtering time, whereas the total intensity of V2p
peaks decreases practically to zero after 20 min. exposure to argon
bombardment indicating that the thickness of vanadium oxide layer is of the
order of several nm. Considerable increase of the ratio of intensities of
the two forms of vanadium ions in the first period of sputtering is in line
with the conclusion that the vanadium oxide layer enveloping the anatase
grains is composed of two parts, form II of vanadium ions being in direct
contact with TiO_2 and form I constituting the upper part. Following
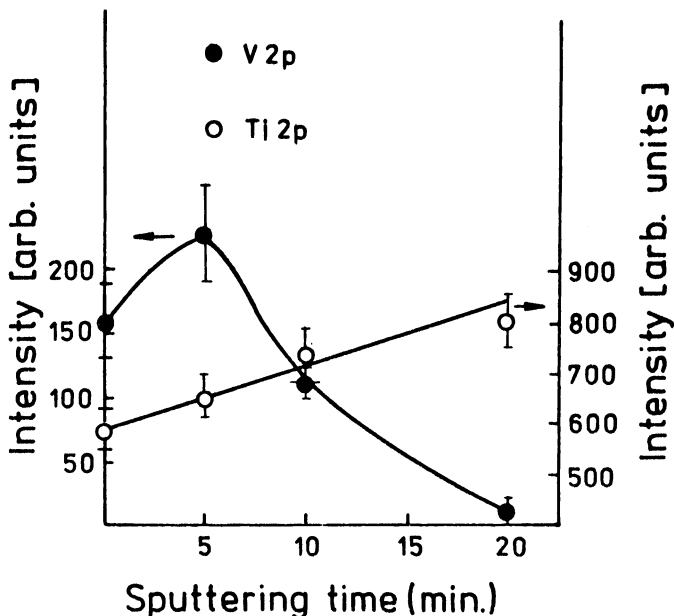mechanism of the migration of vanadium ions over the surface of anatase

Fig. 4 Concentration of vanadium and titanium as function
of time of sputtering. The same sample as in Fig. 3.(Ref. 5)

grains emerges from these experiments. At first a thin probably
monomolecular layer is formed, its properties being strongly modified by
the interaction with the anatase surface, what in higher temperatures
results in the reduction of vanadium ions to a lower valence state. Further
migration of vanadium ions on top of the first layer results in the
formation of a multilayer structure, the outer part assuming the structure
of V_2O_5. The fact that the XPS spectra reveal the presence of the Ti2p peak
of considerable intensity leads to the conclusion that vanadium ions migrate
not over the whole surface of anatase crystallites, but only over certain
crystal planes characterized by appropriate values of surface free energy.

Migration of vanadium oxide over the surface of anatase cannot be due just
to the spreading under the influence of the concentration gradient, as in
identical experimental conditions no migration takes place over the surface
of rutile. The only other driving force which may cause the migration of
V_2O_5 over the surface of anatase is the change in surface free energy, the
migration being the manifestation of a general phenomenon of wetting of one
oxide by another oxide. Such migration will namely take place if the surface
tension of anatase which is the measure of its cohesion energy is greater
than the appropriate sum of the surface tension of V_2O_5 measuring its
cohesion energy and the interfacial tension V_2O_5/anatase, related to the
energy of adhesion of these two solids Fig.(5) . The migration of vanadium
oxide will continue until the film attains such thickness, whereat its
surface free energy does not depend any more on the presence of the TiO_2
support. As the values of cohesion energy vary with the type of crystal
plane, it may be easily explained that wetting takes place only on certain
crystal planes of anatase, other planes remaining exposed to the gas phase.
Even greater differences in the cohesion energy may characterize various
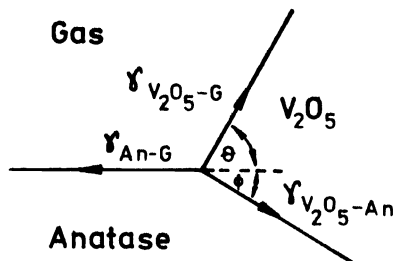
$$\gamma_{An-G} > \gamma_{V_2O_5-G} \cdot \cos\theta + \gamma_{V_2O_5-An} \cdot \cos\phi$$

Fig. 5 Force diagram at V_2O_5 – anatase interface.

polymorphic modifications, as illustrated by the case of anatase and rutile:
vanadium oxide is wetting some crystal planes of anatase, but not those of
rutile.

Table 1 summarizes the interfacial relations in different oxide systems,
which have been studied recently (Ref. 6). It may be seen that V_2O_5 is
wetting not only TiO_2 (anatase), but also ZrO_2 and both γ and α-Al_2O_3
whereas no wetting is observed in the case of SiO_2. Similarly, SiO_2 is not
wetted by MoO_3. It is interesting that at variance with the behaviour of
V_2O_5, MoO_3 is wetting both anatase and rutile, what would imply a much lower
surface energy of MoO_3 as compared to V_2O_5.

TABLE 1. Occurence of wetting in oxide systems

Migrating oxide	Immobile oxide	Temperature K	Wetting
V_2O_5	TiO_2 anatase	823-923	+
V_2O_5	TiO_2 rutile	823-923	-
V_2O_5	ZrO_2 monoclin.	823-923	+
V_2O_5	SiO_2	923	-
V_2O_5	γ-Al_2O_3	923	+
V_2O_5	α-Al_2O_3	923	+
MoO_3	TiO_2 anatase	923	+
MoO_3	TiO_2 rutile	923	+
MoO_3	SiO_2	923	-
MoO_3	Co_3O_4	823	-
MoO_3	Mn_2O_3	823	+

It should be noted that because of the high value of the surface free energy
of many solids the driving force of the surface migration may attain
considerable value and spreading may take place already at relatively low

temperature. As an example Fig. 6 shows the changes of electrical
conductivity on heating to different temperatures and cooling a powder
mixture of MgO and Cr_2O_3 (Ref. 7). It may be seen that already on heating
to 350°C irreversible changes of electrical conductivity are observed
indicating that Cr_2O_3 was spread over the surface of MgO grains.
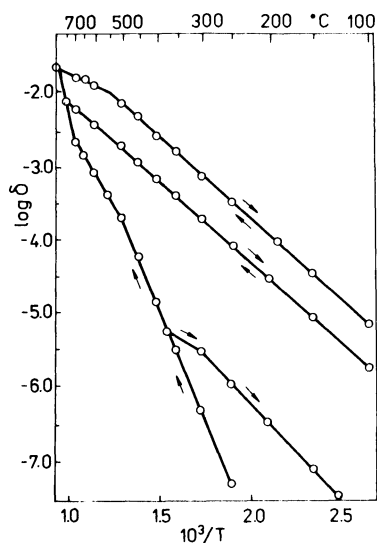

Fig. 6 Changes of electrical conductivity observed on
heating the mechanical mixture of MgO and Cr_2O_3 to different
temperatures and subsequent cooling (Ref. 7).

The phenomenon of wetting of oxides by other oxides is of paramount
importance for the progress of solid state reactions in oxide systems. As an
illustration we shall describe the solid state synthesis of some transition
metal oxysalts. In the case of synthesis of isostructural $CoMoO_4$ and $MnMoO_3$
from MoO_3 and Co_3O_4 or Mn_2O_3 respectively the reactions begin to proceed at
a measurable rate at about 500°C and the parabolic rate law is obeyed
indicating that diffusion is the rate determining step of the reaction (Ref.
8,9), MoO_3 being the attacking reactant. At this point however, the
difference in the behaviour of the two systems should be emphasized: in the
case of the Co_3O_4+MoO_3 system the rate constant strongly depends on the
composition of the reacting mixture, whereas in the Mn_2O_3-MoO_3 system it is
independent of the composition. This difference is due to different rates of
migration of MoO_3 over the surface of Co_3O_4 or Mn_2O_3 grains. In the powder
mixture of Co_3O_4 and MoO_3 the latter is not wetting the former and the
reaction starts only at the intergranular contacts, the reaction interface
being a function of the number of intergranular contacts. The observed
dependence of the rate constant on the composition can be well described by
the equation taking into account the dependence of the number of contacts
between the grains of the two reactants on the composition of the reacting
mixture. On the other hand MoO_3 when mixed with Mn_2O_3, migrates rapidly over
the surface of its grains, enveloping them in a thin overlayer and then
diffusing inwards through the reaction product, formed at the interface. In
these conditions the reaction interface is independent of the number of
intergranular contacts.

Rapid surface migration of oxides over other oxides is in many cases
responsible for the surface properties of oxide systems and is therefore of
fundamental importance in the preparation of catalysts. As an example of the
effect of surface migration on the catalytic properties of oxide systems
Fig. 7 shows the temperature dependence of the catalytic activity of $MgMoO_4$-
$NiMoO_4$ catalysts of different composition in the oxidation of propylene to
acrolein (Ref. 10). The catalysts were obtained by prolonged heating of
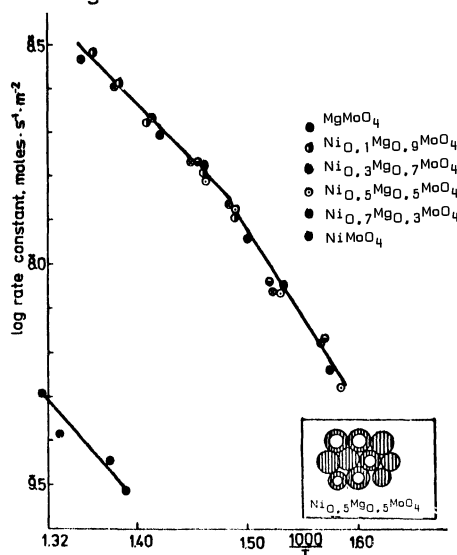mixtures of $MgMoO_4$ and $NiMoO_3$, taken in appropriate proportions, at 700^oC.

Fig. 7 Temperature dependence of the rate constant of the
oxidation of propylene on mixtures of $MgMoO_4$-$NiMoO_4$ of
different composition (Ref. 10)

Activity of $MgMoO_4$ was very low, whereas the activity per BET unit surface
area of all other samples, from those of composition 0.1 $NiMoO_4$ + 0.9 $MgMoO_4$
through Ni : Mg = 0.5 : 0.5 and Ni : Mg = 0.7 : 0.3 to pure $NiMoO_3$ was
practically the same. This indicates that $NiMoO_3$ migrates over the surface
of $MgMoO_3$ grains enveloping them with a thin layer so that the surface of
the catalyst exposed to the interaction with the gas phase reactants, is
composed only of $NiMoO_4$ irrespectively of the composition of the catalyst.
The resulting structure of these catalysts is schematically represented in
the insert in Fig. 7 . This type of structure is very often encountered in
the case of oxide-on-carrier catalysts. One of the most spectacular examples
is the industrially important V_2O_5-on-anatase catalyst for oxidation of
o-xylene to phthalic anhydride. It is now established (Ref. 11) that the
catalyst is composed of grains of TiO_2 covered by a monolayer of V_2O_5, which
constitutes the active and highly selective catalyst.The rest of vanadium is
present in form of V_2O_5 crystallites and serves as a reservoir of vanadium
to replenish those parts of the overlayer, which could be worn off in the
course of the catalytic reaction. Indeed, Fig. 8 shows the results of an
experiment, in which a mechanical mixture of V_2O_5 and anatase was placed in
a reactor and its catalytic activity (curve I) was determined as a function
of the time-on-stream (Ref. 12) . It may be seen that the activity of the
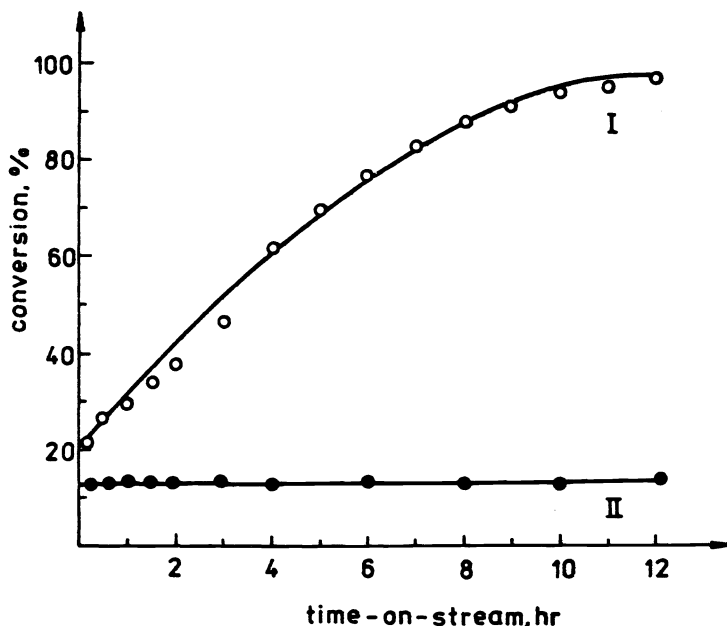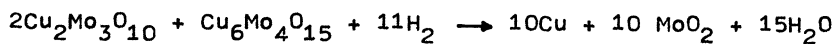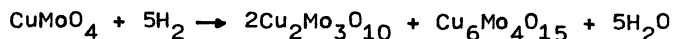catalyst increases gradually in the course of the reaction as a result of

Fig. 8 Catalytic activity in oxidation of o-xylene for the V_2O_5-anatase (curve I) and V_2O_5-rutile (curve II) mechanical mixtures as function of the time-on-stream (Ref. 12).

spreading of V_2O_5 over the surface of anatase in the conditions of the reaction and formation of a monolayer of high activity and selectivity. It is noteworthy that no increase of the catalytic activity is observed in the course of the reaction when a mixture of V_2O_5 and rutile is used (curve II) in Fig. 8). This demonstrates that it is the difference in surface energy which is responsible for the rapid migration of V_2O_5.

Very often the rapid surface migration may explain the dramatic influence of very small amounts of foreign additives on the course of the solid state reactions. In this respect let us discuss the reduction of $CuMoO_4$ in hydrogen (Ref. 13). Fig. 9 shows the degree of conversion α as function of time of the reaction carried out at $420^\circ C$ in 21.5 torr of hydrogen (curve 1). The curve is composed of two parts, corresponding to two consecutive steps of reduction:

$$CuMoO_4 + 5H_2 \longrightarrow 2Cu_2Mo_3O_{10} + Cu_6Mo_4O_{15} + 5H_2O$$

$$2Cu_2Mo_3O_{10} + Cu_6Mo_4O_{15} + 11H_2 \longrightarrow 10Cu + 10 MoO_2 + 15H_2O$$

It should be emphasized that this is an interesting example of a consecutive reaction, in which the second step is much faster than the first one. Namely metallic copper formed as the result of consecutive reduction of the intermediate products serves as sites responsible for a very rapid activation of molecular hydrogen. However no metallic copper can appear before the whole initial amount of $CuMoO_4$ becomes converted to the intermediate products, because it reacts with $CuMoO_4$. Once the latter disappears, metallic copper starts to be formed and accelerates the activation of hydrogen so that the second step of the reaction can proceed
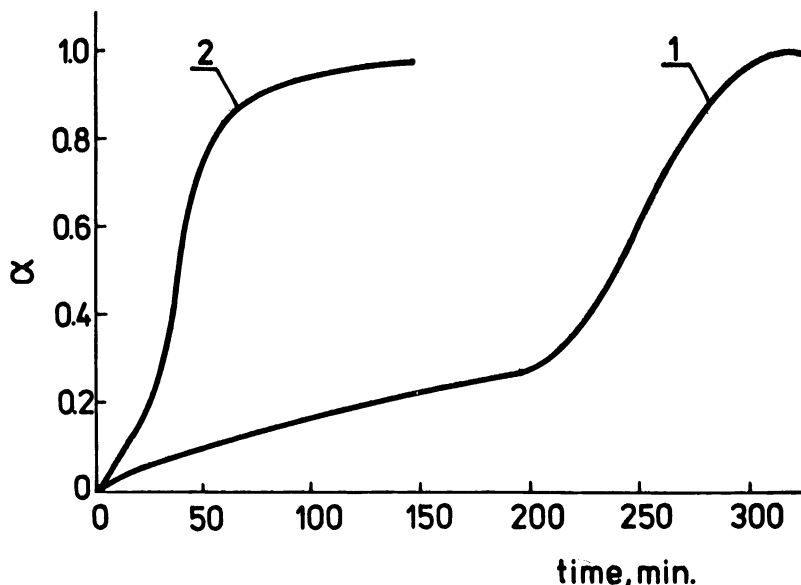
much faster than the first one.

Fig. 9 Degree of reduction in 21.5 Torr of hydrogen at
$418^{\circ}C$ as function of time for: 1 - pure $CuMoO_4$, 2 - $CuMoO_4$ +
1% MoO_3 (Ref. 13)

Completely different behaviour is observed when small amounts of different
additives are mixed with $CuMoO_4$. Curve 2 in Fig. 9, shows the kinetics of
the reduction of $CuMoO_4$ with 1% of MoO_3. It may be seen that addition of
MoO_3 even in such small amount as 1% increases the rate of the first step
of the reduction of $CuMoO_4$ by more than one order of magnitude. One of the
hypothesis which may explain these observations is the assumption of a very
rapid migration of MoO_3 which in the very initial stage of the reaction
could spread uniformly over the surface of $CuMoO_4$, generating on reduction a
large number of MoO_2 centers for activation of hydrogen and facilitating in
this way the surface redox processes.

In many instances the two limiting cases of the kinetics of solid state
reactions, shown in Fig. 1 and 2 are not due to transport phenomena but to
chemical factors. As already mentioned, in the case of reactions, in which
a solid reacts with another solid, liquid, or gas, nucleation takes place at
the surface of the crystallites of the "attacked" solid, the nuclei being
preferentially formed at certain surface sites called potential nucleation
centers. Formation of a nucleus at such center may perturb the surface in
its vicinity, increasing its reactivity. The zone of increased reactivity
will thus move along with the growing nucleus. In such case a preferential
growth of the nuclei will be observed, once they are formed. This phenomenon
is called "autolocalization" and gives rise to the kinetics analogous to
that illustrated in Fig. 1a and 2a. Conversely, when the nuclei do not exert
any influence on their surrounding, the reactivity of the surface is uniform

and the whole surface of the crystallites may become the reaction interface.
The course of the reaction may be then represented by a model analogous to
that shown in Fig. 1b and 2b.

The role of potential nucleation centers may be played by surface sites,
whereat the strict periodicity of the lattice potential is perturbed. This
may be caused by the presence of many various defects of the surface, such
as:
- point defects (vacancies, interstitial ions, altervalent ions, foreign
ions),
- extended defects (dislocations, shear planes),
- three dimentional defects (steps, kinks, etc.),
- adsorbed species.

All these defects may be generated or annihilated by an appropriate
treatment of the surface such as outgassing or adsorption of different
molecules, prereduction or preoxidation, irradiation, impregnation with
foreign ions or their implantation, mechanical treatment, thermal processing
etc. It should be emphasized that the pretreatment of the surface is one of
the most powerful methods of controlling the rate of solid state reaction.
It may be applied either to activate the solids and increase the rate of a
solid state reaction in the case when synthesis of a given product is the
objective, or to dezactivate the solid in order to stabilize the surface
structure against such processes as ageing, wearing etc.

When discussing the influence of the pretreatment on surface properties it
should be borne in mind that the surface layer of the crystallite may have
different physical and chemical properties than its bulk. It is now well
established that e.g. the surface composition of the solid is in general
different from the composition of the bulk (Ref. 14-16) due to the important
contribution from the surface free energy to the condition of the
thermodynamic equilibrium. We are namely used to discuss the adsorption at
the gas-solid or liquid-solid interface from the position of the gas or
liquid phase and we are accustomed to treat this phenomenom as the
increased concentration of one of the components of the gas or liquid
solution at the interface. However, the interface has two sides and the
same phenomenon of adsorption takes place at this interface from the side of
the solid, if the solid is a solid solution. This results in the increased
concentration of one of the components of the solid solution at the
interface, its surface excess being described by the Gibbs adsorption
equation. This phenomenon operates even in case of pure oxides, because
they usually are nonstoichiometric compounds which may be considered as
solid solutions of defects in the lattice. When the surface concentration of
defects exceeds certain critical value, their ordering may take place at
the surface, resulting in the formation of new surface phases. As shown by
Nowotny (Ref. 17) the mobility of cations in the surface layer of oxides
may be by orders of magnitude higher than their mobility in the bulk so that
equilibration of the surface layer of an oxide with gas phase oxygen, and
the resulting reconstruction of the surface layer or formation of new

surface phases may be very fast.

It should be remembered that due to the contribution from the surface free
energy the values of the Gibbs free energy, whereat a given phase
transformation occurs at the surface may be different from that required for
this transformation to take place in the bulk of the crystal. When an oxide
may form two different polymorphic modifications, the phase transformation
on heating may take place at the surface long before the temperature is
attained, whereat this transformation in observed in the bulk of the
crystallites. The crystallites are then composed of the bulk having the
structure of one polymorphic modification, enveloped by a surface layer of
a structure characteristic for the other modification. As an example let
us discuss the behaviour of cobalt molybdate $CoMoO_4$. Under normal pressure
this compound forms two polymorphic modifications (Ref. 18): the low
temperature green modification "b" in which molybdenum is in tetrahedral
coordination and the high temperature violet modification "a" with
molybdenum in octahedral sites. The transition takes place at $420^{\circ}C$. XPS
studies of this system revealed however that on heating modification "b" its
surface becomes reconstructed already at $250^{\circ}C$, the reconstruction being
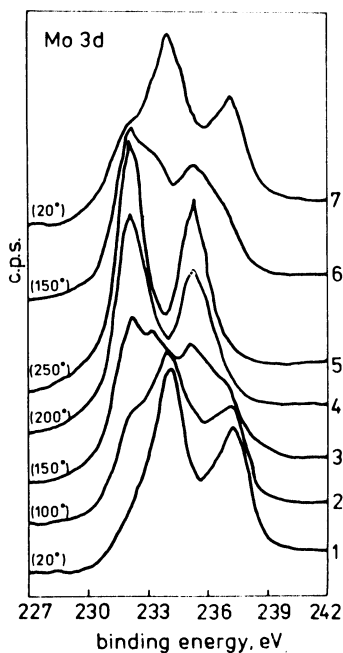fully reversible (Ref. 19). This is illustrated in Fig. 10, in which the

Fig. 10 Changes of the photoelectron spectra in the region
of the Mo3d core level of the sample of $CoMoO_4$ on heating
and subsequent cooling (Ref. 19)

photoelectron spectra of Mo3d electrons from modification "b" of $CoMoO_4$ are
shown at different stages of heating and cooling the sample. At normal
temperature the Mo3d doublet is visible at 234.2 and 237.2 eV. On heating
the sample a shift of this doublet to lower values of binding energy started
to be visible around $100^\circ C$, and at $200^\circ C$ the doublet assumed a new position
at 232.2 and 235.3 eV, which did not change on further heating to higher
temperatures. When the sample was cooled again to room temperature, the
shift of the Mo3d doublet was observed back to the initial value. It should
be noted that on heating above $390^\circ C$ reduction of the sample began to be
perceptible. It may be assumed that the shift of Mo3d peak reflects the
reversible polymorphic transformation, which at the surface takes place at
the temperature $300^\circ C$ lower than in the bulk. A general conclusion may be
thus formulated that not only the chemical composition of the surface layer
but also its structure is very often different from that of the bulk.

As the last important factor we would like to mention the effect of the
interaction of solids with the gas phase. Experimental evidence accumulated
in recent years indicates that composition of the gas phase may have a
profound influence on the structure of the surface, and hence on the
properties of the solid and its reactivity. It has been shown above that due
to the contribution from the surface free energy the composition of the
surface of the solid differs from that of the bulk. As however the surface
free energy depends on the composition of the gas phase, it may be expected
that changes of the latter will entail changes of the surface composition.
This may be particularly pronounced in case of adsorption of molecules of
surface active compounds. In the case of transition metal oxides changes of
the defect equilibria will simultaneously take place, influencing also the
surface composition. This may result in a number of different phenomena such
as ordering of defects at the surface, transformations of surface structure
and formation of new bidimensional surface phases. They may entail the
appearance of new types of potential nucleation centers, considerable
changes of the mobility of lattice elements at the surface, modification of
the electrical surface double layer, shift of the chemical potential of
electrons Fermi level and many other effects - all of them having a
profound influence on the reactivity of solids.

REFERENCES

1. B. Delmon, Introduction a la cinetique heterogene Editions Technip, Paris
   (1969)
2. J. Haber, Proc. 9th Intern.Symposium Reactivity of Solids, Kraków 1980,
   ed. K. Dyrek, J. Haber, J. Nowotny, Elsevier(1982) p. 3
3. V.V. Boldyrev, M. Bulens, B. Delmon, The Control of the Reactivity of
   Solids, Elsevier(1979)
4. J. Haber, in "Surface Properties and Catalysis by Non-metals", ed. J.P.
   Bonnelle, B. Delmon, E. Derouane, D. Reidel,(1983), p. 1
5. J. Haber, T. Machej, T. Czeppe, in print
6. T. Machej, to be published

7. J. Dereń, J. Haber, J. Electrochem. Soc. 113, 1349 (1966)

8. T. Bąk, J. Haber, J. Ziółkowski, Bull. Acad. Polon. Sci., ser. sci. chim. 19, 489 (1971)

9. J. Haber, J. Ziółkowski, Proc. 7th Intern. Symp. Reactivity of Solids, Bristol 1972, ed. F.S. Stone, Chapman and Hall Ltd., London (1972), p. 782

10. J. Haber, E. Mielczarska, J. Turek, in print

11. M. Gąsior, I. Gąsior, B. Grzybowska, Appl. Catal. 10, 87 (1984)

12. M. Gąsior, Ph. D. Thesis, Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków (1984)

13. J. Haber, E. Jamroż, Rev. Chim. Minerale 20, 712 (1983)

14. W.M.H. Sachtler, R.A. van Santen, Appl. Surface Sci. 3, 121 (1979)

15. J. Haber, Z. Chem. 16, 421 (1976)

16. J. Nowotny, I. Sikora, J.B. Wagner Jr., in "Transport in Non-Stoichiometric Compounds", ed. J. Nowotny, PWN Warsaw - Elsevier Amsterdam (1982), p. 244

17. J. Nowotny, J. Materials Sci. 12, 1143 (1977)

18. J. Chojnacki, J. Haber, R. Kozłowski, J. Solid State Chem. 11, 106 (1974)

19. J. Haber, J. Stoch, L. Ungier, Proc. 6th Czechoslov. Conf. on Electronies and Vac. Phys., ed M.Vesely, J. Breza, R. Harman, Slovak Techn. Univ. Bratislava (1976), p. 98